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AUTHOR(S):

Sato, Naoki; Yoshida, Hiroyuki; Tsutsumi, Kiyohiko

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Photoemission and Inverse Photoemission Studies on Organic Semiconductor Thin Films

Naoki Sato, Hiroyuki Yoshida and Kiyohiko Tsutsumi

Ultraviolet photoemission (PE) and inverse photoemission (IPE) spectra were measured for evaporated thin films of perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA) and *N,N'*-dimethylperylene-3,4,9,10-bis(dicarboximide) (DM-PBDCI), the latter known as an *n*-type organic semiconductor and the semiconducting nature of the former still unidentified. The electronic structure around the energy gap, obtained from the combination of PE and IPE spectra observed, turns out to be almost common between the two compounds, indicating that PTCDA could be grouped into the *n*-type semiconductor.

Keywords : Photoemission/ Inverse photoemission/ Organic semiconductor/ Thin film/ PTCDA

The reliable information of the electronic structure of both occupied and unoccupied states, in particular, around the energy gap, is indispensable for the elucidation of electronic properties of solids and/or the design of new electronic materials. Ultraviolet photoemission (PE) spectroscopy is widely known as one of the most useful methods to obtain direct information of valence electronic structure in solids, even in the case of organic ones, and, in contrast, there has been no efficient method to observe directly their unoccupied states. However, inverse photoemission (IPE) spectroscopy has largely been developed as a method to detect such states very recently. In this context we have built an apparatus for the purpose of IPE measurements in the vacuum ultraviolet region particularly for organic solids and have so far applied it to thin films of a few organic semiconductors.

On the one hand, perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA) is one of organic semiconductors, often used as a material in the studies viewing the

development of so-called molecular electronic devices, while its electronic nature has not completely been clarified, in particular, about the semiconducting behavior as *n*- or *p*-type. Here, *N,N'*-dimethylperylene-3,4,9,10-bis(dicarboximide) (DM-PBDCI) is its analogous compound and has already been confirmed to be an *n*-type organic semiconductor from several different experiments. In this work, PE and IPE spectra were measured for evaporated thin films of PTCDA and DM-PBDCI to compare their valence and lower vacant electronic structures for checking the semiconducting characteristics of PTCDA.

The sample materials were purified by repeated sublimation at a pressure lower than 5×10^{-5} Pa. The specimen films of PTCDA and DM-PBDCI were deposited at a thickness of 3-20 nm on polycrystalline copper substrates and were measured in situ on two separate home-built apparatus, each for PE or IPE. The apparatus for PE measurements was an upgraded version

INTERFACE SCIENCE — Molecular Aggregates —

Scope of research

The research at this subdivision is devoted to correlation studies on structures and properties of both natural and artificial molecular aggregates from two main standpoints: photoelectric and dielectric behaviors. The electronic structure of molecular and/or polymeric thin films is studied using photoelectron spectroscopies in connection with the former, and its results are applied to create novel molecular systems with characteristic electronic functions. The latter is concerned with heterogeneous structures in microcapsules, biopolymers, biological membranes and biological cells, and the nonlinearity in their dielectric properties is also studied in relation to molecular motions.



Professor
SATO, Naoki
(D Sc)



Associate Professor
ASAMI, Koji
(D Sc)



Instructor
KITA, Yasuo
(D Sc)



Instructor
YOSHIDA, Hiroyuki
(D Sc)

Students

ODA, Masao (DC)
SAKUMA, Taro (DC)
YANO, Setsuko (MC)
SHIMADA, Kenji (MC)
TSUTSUMI, Kiyohiko (MC)
NAGAI, Yasuaki (MC)

of that reported in detail previously [1]. That for IPE, consisting of two ultra-high vacuum chambers, was equipped with an Erdman-Zipf type gun supplying an electron beam of a particular kinetic energy distribution in the range from 4 to 15 eV and a bandpass detector with the maximum sensitivity at 9.8 eV fabricated from a Cu-BeO photomultiplier as well as optical crystal plates; such a combination of the electron gun and the detector lead to an overall energy resolution of about 0.8 eV. Reliable IPE spectra, free of charging and/or radiation damage, were obtained in a few tens of minutes after starting irradiation on a specimen film.

Ultraviolet PE spectra of DM-PBDCI and PTCDA measured using the same excitation energy were very similar to each other. Such spectra, recorded by using a spherical retarding-field analyzer, permitted to determine accurate values of threshold ionization energy and work function, to be $I_s^{\text{th}} = 6.1_5$ eV and $\phi = 4.4_1$ eV, respectively, for PTCDA and to be $I_s^{\text{th}} = 6.1_0$ eV and $\phi = 4.5_6$ eV, respectively, for DM-PBDCI. The good correspondence observed for the energy parameters as well as the spectral lineshapes indicates that the electronic structure in the valence electronic states is largely common for the two compounds in the thin films.

IPE spectra of DM-PBDCI and PTCDA thin films were obtained to be almost the same under the given spectral resolution. This suggests that the electronic structure in lower unoccupied states is also common for the two compounds. Besides, the spectrum of PTCDA can be compared with the recent result by Hirose et al. [2]; the two independent spectra are regarded to essentially

coincide with each other.

Semiempirical MO calculations using the PM3 method showed that most MOs around the energy gap for both molecules are predominantly characterized by the perylene skeleton, so that the corresponding MOs for them are of almost identical nature. This supports that almost the same electronic structure observed for the two films for both highest occupied and lowest unoccupied states can basically be understood, on the basis of the polarization model of the electronic structure in organic molecular solids.

The combinations of the respective PE and IPE spectra obtained for PTCDA and DM-PBDCI show the resemblance of the electronic structure around the energy gap for both compounds, and it is notable that the Fermi level could be positioned close to the edge of the unoccupied states, by considering the values of work function above. These observations lead, therefore, to the conclusion that the semiconductive characteristics of the two compounds are largely common, so that both could be of *n*-type; this corresponds to the results of charge carrier mobilities in both crystals.

References

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Electrical and Morphological Changes of Human Erythrocytes under High Hydrostatic Pressure Followed by Dielectric Spectroscopy

Koji Asami

Dielectric spectroscopy was applied for studying electrical and structural properties of human erythrocytes under high hydrostatic pressure, which revealed that erythrocytes undergo a change of cell shape, hemolysis, vesiculation and membrane thinning at pressure ranging from 3000 to 5000 atm.

Keywords : Dielectric spectroscopy/ Biological cell/ Hydrostatic pressure/ Membrane

It is well known that biological cells are damaged and killed by high hydrostatic pressure. However, the underlying mechanism has not been clearly understood. This is because there are few studies on properties of cells under high hydrostatic pressure, although many kinds of cells treated by high hydrostatic pressure have been studied at atmospheric pressure. Dielectric spectroscopy that can elucidate electrical and structural properties of cells in non-invasive way is suited for in situ measurements under high hydrostatic pressure because it needs only a pair of electrodes for measurements, which are easily installed in a pressure cell.

Dielectric relaxation spectra have been measured on suspensions of three types of human erythrocytes (normocyte, spherocyte and ghost) under high hydrostatic

pressure up to 5000 atm. Around 3000 atm a change of the cell shape from biconcave to spherical occurred accompanying with hemolysis, which was suggested from the sharpening of the relaxation spectra. At pressure between 3000 and 4000 atm, a new dielectric dispersion appeared at frequencies below 30 kHz, which could be due to microvilation followed by vesiculation. At 5000 atm, the capacitance of the plasma membrane increased, which may indicate thinning of the lipid bilayer and/or intrusion of water into the lipid bilayer.

The present results demonstrated that dielectric spectroscopy is a useful tool for in situ and real-time monitoring of cells under high hydrostatic pressure and can contribute to better understanding of the effects of pressure on cells.